



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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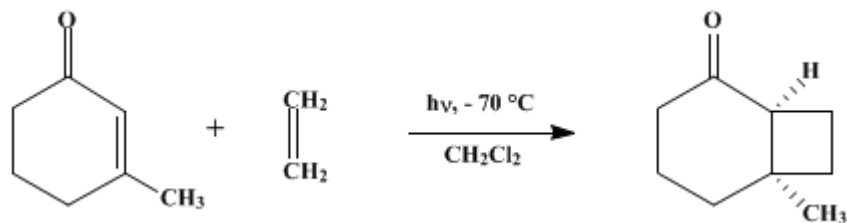
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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PHOTOCYCLIZATION OF AN ENONE TO AN ALKENE: 6-METHYLBICYCLO[4.2.0]OCTAN-2-ONE

[Bicyclo[4.2.0]octan-2-one, 6-methyl-]



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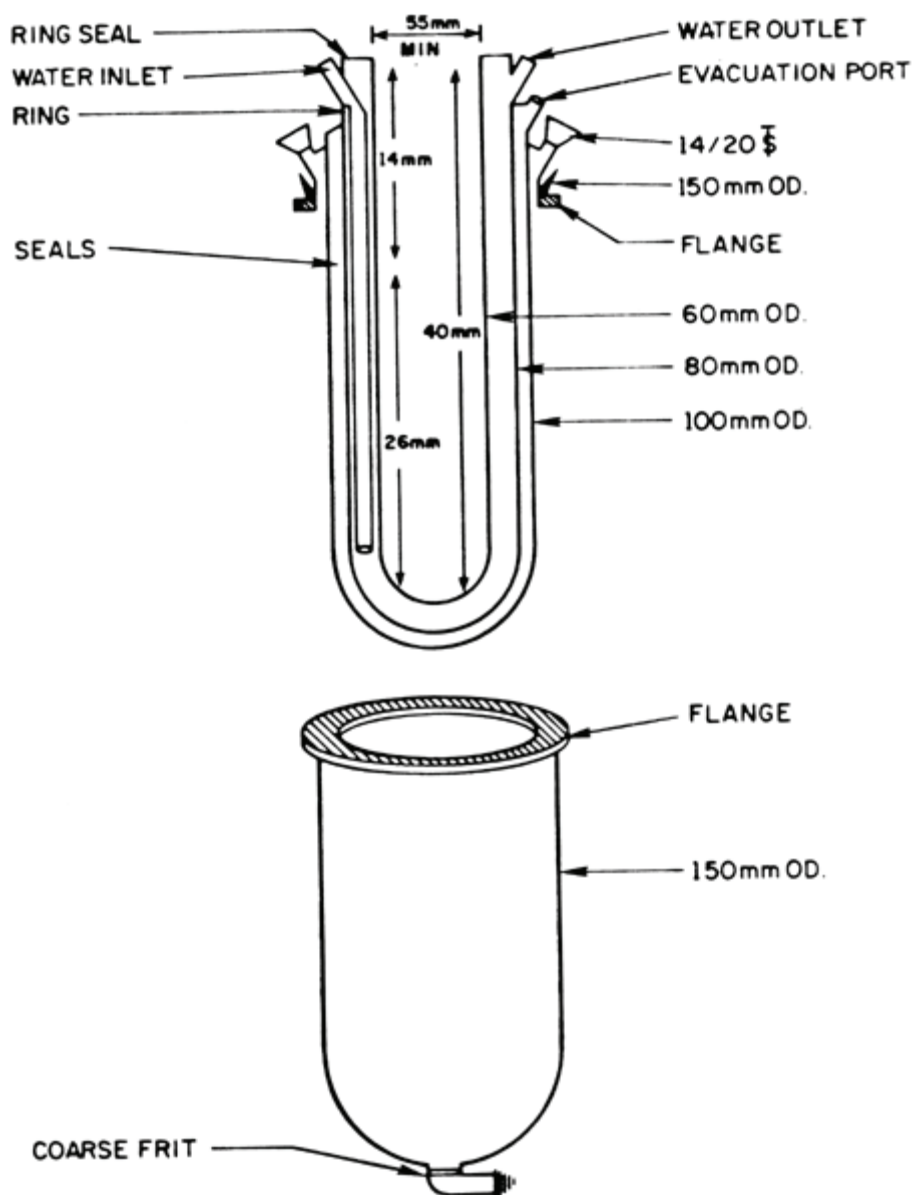
1. Procedure

The irradiation apparatus (Note 1) is charged with a solution of 25.0 g (0.277 mol) of 3-methyl-2-cyclohexenone (Note 2) in reagent-grade dichloromethane (Note 3). A gas outlet tube to an efficient hood is placed in one 14/20 standard taper joint; in the other, there is a stopper that can be removed for periodic sampling. The cooling water is turned on (Note 4) and the apparatus is immersed in a dry-ice/2-propanol bath while the chilled solution is saturated with ethylene (Note 5). The lamp is inserted into the well and turned on (Note 6). Progress of the irradiation is conveniently followed by gas chromatography (Note 7). After about 8 hr, most of the starting material has reacted. At this time, the lamp is turned off and the apparatus removed from the cooling bath. The reaction mixture is degassed with a slow stream of nitrogen while it warms to room temperature, dried over magnesium sulfate, and concentrated with a rotary evaporator at a temperature below 30°C (Note 8). The product is isolated by distillation to afford 27–28 g (86–90%) of 6-methylbicyclo[4.2.0]octan-2-one, bp 62–65°C (3.5 mm) (Note 9) and (Note 10).

2. Notes

1. The apparatus is similar to one described earlier.² A triple-walled Dewar is constructed of Pyrex according to Figure 1. For further discussion concerning this immersion well, contact Joel M. Babbitt, Glassblower, Department of Chemistry, University of South Carolina, Columbia, SC 29208. The evacuated jacket permits the safe use of circulating tap water as a lamp coolant even when irradiations are conducted in a dry ice bath. A further advantage is that three layers of Pyrex constitute an effective filter for light in the 280–300-nm region so that secondary photolysis of cycloadducts is not usually observed. The irradiation flask is a cylindrical vessel of suitable volume fitted with a coarse, fritted disc for gas dispersion and a flanged lip. The light source is either a GE H1000-A36-15, Westinghouse H-36GV-1000, or equivalent lamp with the outer globe removed, used in conjunction with a GE 35-9627-6009 ballast. These lamps are available from the General Electric Company, Lamp Division, Charlotte, North Carolina.

Figure 1. Irradiation vessel.



2. This material can be purchased from Aldrich Chemical Company or prepared from Hagemann's ester.³
3. The volume of solution will vary depending on the exact volume of the apparatus, the temperature, and the miscibility of gaseous reactant in the solvent. The solution should completely surround the lamp, but should not overflow the vessel. The submitters used a volume of 1100 mL, and the checkers used 200 mL.
4. If the flow of cooling water is stopped while the apparatus is cold, the water may freeze and crack the immersion well. The vacuum jacket provides greater insurance against this problem than is available in the commercially available wells used with the usual 450 watt lamps.²
5. CP-grade [ethylene](#) (Matheson) was used without purification. A flow of ca. 100 mL/min of [ethylene](#) for 2–3 hr is adequate for saturation. Gas flow is continued throughout the irradiation in order to maintain a high concentration of [ethylene](#) and for stirring.
6. The lamp will not start if it is too cold or too hot. The practice of blowing [nitrogen](#) over the lamp to remove [ozone](#) is not recommended as this cools the lamp and decreases its output significantly, resulting in an unnecessarily long irradiation period.
7. The submitters used a Varian 1200 FID chromatograph with a 7% Carbowax 20 M on Chromosorb Q, 8-ft × 0.125-in. column, a carrier gas (N₂) flow rate of 40 mL/min; column, 160°C; injector, 220°C; and detector, 215°C. Retention times were [3-methyl-2-cyclohexenone](#), 4.2 min, and [6-methylbicyclo](#)

[4.2.0]octan-2-one, 3.9 min, respectively.

8. If the solvent is removed without care, a considerable amount of volatile product may be lost.

9. This material is contaminated with ~ 10% of 3-methylcyclohexenone. Material of greater purity can be obtained by extending the time of irradiation, carrying out an efficient distillation of product, or decomposing starting material with potassium permanganate prior to distillation.

10. The product has the following spectral properties: IR (CCl₄) cm⁻¹: 1700; ¹H NMR (CCl₄) δ: 1.21 (s, 3 H, methyl), 1.9 (m, 11 H, all other protons); ¹³C NMR (C₆D₆) δ (based on δ C₆D₆ 128.00): 211.63, 51.34, 40.86, 39.45, 35.26, 31.20, 28.84; 21.45, 20.35; mass spectrum (*m/e*) 138.1041 (parent ion).

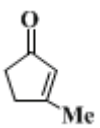
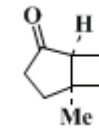
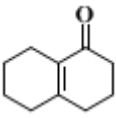
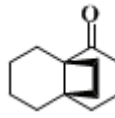
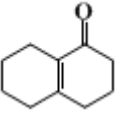
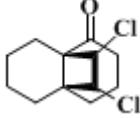
3. Discussion

Although photochemical cycloadditions have gained acceptance in synthetic chemistry,⁴ most such reactions are limited to a relatively small scale. The use of a 1000-W street lamp permits the irradiation of up to 1 mol of substrate in less time than 0.2 mol can be irradiated with the conventional 450-W lamps. Thus, under optimum conditions, the submitters were able to add ethylene to 3-methylcyclohexenone on a 20-g scale in 48 hr (80%) with a 450-W lamp; with the apparatus described here 94 g of this enone was condensed with ethylene in 8 hr (91%).

Some general points regarding photochemical cycloadditions deserve mention: (1) since the reaction is first-order in olefin, the concentration of olefin (especially gaseous olefins) is of critical importance; therefore, the cycloadditions are carried out at low temperature (in some cases, however, low temperature can be detrimental⁵); (2) since lamp output deteriorates with lamp age, the rates of otherwise identical cycloadditions are unlikely to be the same; therefore, it is of critical importance that the progress of each photochemical reaction be followed by some suitable means (GLC, IR, UV, NMR, etc); and (3) as long as all the incident light of appropriate wavelength is absorbed by the enone, the reaction proceeds at a rate independent of enone concentration; thus, the highest concentration of enone at which dimerization can be avoided is optimal.

Several examples of preparative cycloadditions are listed in Table I.

TABLE I
PREPARATIVE-SCALE CYCLOADDITIONS

Entry	Enone	Weight (g)	Olefin	Time (hr)	Product(s)	Yield (%)	Ref.
1.		25	C ₂ H ₄	12		90	6
2.		10	C ₂ H ₄	6		71	7
3.		20	ClHC=CHCl	10		93 ^a	8

^aA mixture of cis and trans olefins was used; a mixture of diastereomeric products was obtained. Both olefins give similar mixtures.

References and Notes

1. Department of Chemistry, University of South Carolina, Columbia, SC 29208. Present address:

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

potassium permanganate (7722-64-7)

nitrogen (7727-37-9)

ethylene (9002-88-4)

dichloromethane (75-09-2)

ozone (10028-15-6)

magnesium sulfate (7487-88-9)

3-methyl-2-cyclohexenone,
3-methylcyclohexenone

6-Methylbicyclo[4.2.0]octan-2-one,
Bicyclo[4.2.0]octan-2-one, 6-methyl- (13404-66-5)